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ELECTROBLEACHING OF COTTON FABRICS IN SODIUM CHLORIDE SOLUTION

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Abstract: *The objective of the paper is to describe an alternative method based on electrochemistry to bleach cotton fabrics. Electrolysis of cotton fabrics soaked in proper electrolyte as a bleaching technology has been studied in this work. Some experiments have been conducted by applying this technique to see the whiteness index effect on fabric cotton. The duration of every experiment was two hours, and it has been applied different currents to study the whiteness index, as well as wetting agent has been used. Once the optimal conditions have been established, a treatment with reuse of the electrolyte and wetting agent has been carried out and six samples have been analysed in these conditions. It has been observed how the cotton fabric was bleaching with the same electrolyte and the whiteness index was similar every time and better than the conventional treatment. In addition, resistance and surface morphology did not present any noticeable weakness at fabrics submitted to electrolysis*

Keywords: *electrobleaching, whiteness index, cotton fabrics, sodium hypochlorite.*

1 INTRODUCTION

Raw cotton fibers contain a certain amount of natural non cellulosic impurities, such as proteins, wax, fats, pectins hemicelluloses and mineral matter, distributed on their peripheral layers, either the cuticle or the primary wall. In addition to these non cellulose components, raw fibers also contain some colouring matter of uncertain and complex chemical composition that confers a typical yellowish-brown colour. All these components render the cotton fibers hydrophobic and impair effective and uniform dyeability and successful processing into finished apparels.

To avoid the unwanted effects of non-cellulosic constituents, they are removed in a series of pre-treatment or preparation steps prior to the application of further finishing steps like dyeing or printing. One of the central operations in preparation treatments of raw cotton fabrics is bleaching. Conventional techniques for bleaching of cotton are based on oxidative processes. One of them, which was developed long time ago, is chlorine bleaching. This process consists of a batch or pad immersion of the fabric in a solution containing sodium hypochlorite or other oxidizing chlorine compound. This technique has several advantages, like low chemical costs and no heating costs, because it works an ambient temperature. However, it has several disadvantages because it requires the transport, storage and handling of hazardous, unstable chemicals and hence it poses stringent industrial safety and risk prevention concerns.

Electrobleaching is based on the application of a DC voltage between two electrodes in an electrochemical cell to enable the passage of a DC current through an ion conducting medium (the electrolyte) that separates the electrodes. Electrochemical technologies show a unique combination of advantageous features because they can be conveniently operated in situ with inexpensive equipment, at ambient temperature and pressure, with low energy consumption and short time requirements, just by using electrons as the only reagent or driving force [1]. Moreover, these technologies can be advantageously connected and supplied with renewable energies. In the present study, the electrochemical system is devised to electrogenerate the desired oxidants in situ to address more controlled oxidation reactions (indirect electro-oxidation) with high efficiency [2]. As a result, bleaching can be performed without adding oxidants, avoiding their transportation, handling, storage and the generation and management of additional by-products.

The potential application of electrochemical techniques for bleaching fabrics has been reported by Kokot et al. [3] and Fukatsu et al. [4] who analysed bleaching and structural damage in cotton fibers electrolysed using Pt electrodes in alkaline solutions containing Na_2SO_4. The effect was attributed to the formation of hydroxyl radicals at both the anode and cathode during the oxygen electrogeneration and the reduction of dissolved oxygen respectively. Also, Fukatsu et al. [5] studied the electrochemistry decoloration of dyed cotton fabrics using a platinum anode. A significant decoloration was observed only when the electrolysis was conducted in a potassium chloride solution, which was attributed to the electrogeneration of hypochlorite. The generation of strongly oxidizing hypohalogenites from electrolysis of solutions containing sodium chloride and potassium bromide was also investigated as a mean for bleaching indigo-dyed denim fabrics [6, 7]. The oxidants were produced on site in an undivided electrolyzer at high current efficiency. The electrolyzer was coupled to a commercial drum washing machine, which received an inflow of the electrogenerated bleaching liquor. The electrogeneration of chlorine compounds has also been proposed as a viable technology for delignification and bleaching of wood pulp in the paper industry [8]. However, to the best of our knowledge, an exhaustive study of bleaching of undyed raw cotton fabrics by chlorine active species generated in situ by electrolysis from a chloride-containing electrolyte has not been carried out to date.

When a chloride-containing electrolyte is electrolyzed by passing through a proper DC current between two electrodes in an undivided electrochemical cell, a set of chlorine-containing oxidants are anodically produced by the oxidation of chloride ions and released into the bulk of the solution according to the following reactions [2]:

Anode:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

Solution:

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \tag{2}$$

$$HClO \leftrightarrow H^+ + ClO^- \tag{3}$$

While hydrogen and hydroxyl ions are formed at the cathode by the half-reaction:

Cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{4}$$

The equilibrium outlined in Eq. (3) depends on the pH of the bulk solution, as shown in Figure 1 [9]. Hypochlorous acid is rapidly converted into hypochlorite by reacting with hydroxyl ions from the cathode according to reaction in Eq. 5, which predicts a self-adjusted pH in the region of predominance of the hypochlorite ion:

$$HClO + OH^- \rightarrow ClO^- + H_2O \tag{5}$$

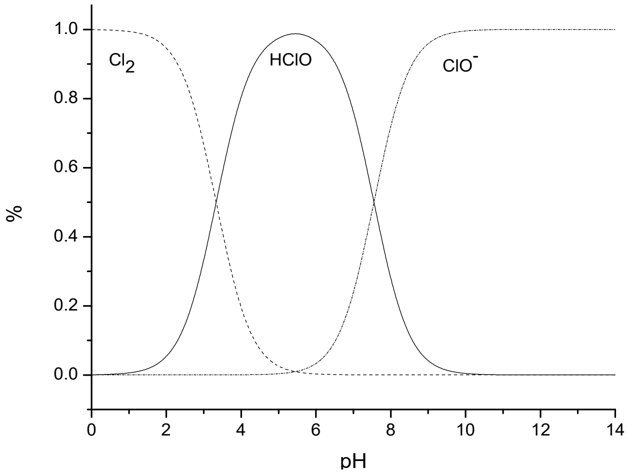

Figure 1 Distribution of main aqueous chlorine species as a function of pH at 25ºC

One further advantage of the electrobleaching technology based on the hypochlorite electrogeneration over conventional chemical bleaching is the exhausted liquor can be easily regenerated because reaction of hypochlorite with colouring matter and other non-cellulosic impurities mostly gives back the precursor chloride ions:

$$\begin{aligned} &ClO^- + H_2O + Coloured\ Matter \rightarrow \\ &\rightarrow Cl^- + 2OH^- + Bleached\ Matter \end{aligned} \tag{6}$$

Instead, in a conventional bleaching process, hypochlorite must be replenished as it is exhausted, so leading to higher chemical costs and/or discharging higher amounts of wastewaters with higher pollutant loads.

In this work we report the bleaching of woven raw cotton fabrics by hypochlorite liquors electrogenerated on site upon passing a DC current through a sodium chloride electrolyte. Several sample fabrics were successively processed in batchwise mode in the same electrolytic bath and the change in whiteness index measured. The influence of adding a wetting agent at very low concentration was analysed. Furthermore, the effect of the electrobleaching process on the tensile strength and the surface morphology of the cellulose fiber was examined. Similar properties were measured for fabrics submitted to conventional bleaching steps by chemical bleach liquors for the sake of comparison.

2 EXPERIMENTAL

The electrochemical generation of the bleaching oxidants was conducted in a filter-press electrochemical cell, which has been used in previous work by our group [10–12], with an electrode projected area of 100 cm^2.

The anode was a commercial DSA® electrode, composed of a coating of mixed metal oxides, namely, titanium oxide (TiO_2), iridium oxide (IrO_2) and ruthenium oxide (RuO_2), on a Ti support in the form of expanded mesh. This kind of anodes are known to have very good electroactivity for chlorine evolution as well as excellent long-term mechanical and chemical stability [2]. The cathode was a stainless steel plate electrode.

A sodium chloride (Carlo Ebra Reagents, 99.5%) solution of concentration 0.34 M was used as the supporting electrolyte. Leophen RA by BASF was used as the wetting agent. It has used a concentration of 0.02% v./v. at electrochemical treatment and 0.2% v./v. at conventional treatment. The volume of solution was 1000 mL. Active (free) chlorine production was measured with Spectroquant® test kits by Merck [13].

The fabric used was a 100% cotton twill fabric with 210 g/m^2, the initial whiteness index of this raw cotton fabric was 16.41.

The experiments were carried out under galvanostatic conditions using a DC power supply model BL Ausonic FA-325. The applied current was 0.5 and 1.0 A. All electrolyses were run at a self-adjusted pH of 9-9.5 and at 25°C. Up to six pre-washed unscoured cotton fabric samples were processed consecutively in a batch mode for a total duration of two hours each.

For the sake of comparison, raw cotton fabric samples were bleached by conventional chemical treatment consisting of a soaking in bleach (at concentration of 3 g/L) during two hours in alkaline medium at room temperatre. After bleaching, fabrics were submitted to antichlor treatment, washed repeatedly up to neutral pH and dried at 60°C.

The surface morphology of raw and bleached cotton samples were examined by scanning electron microscope (SEM: JEOL JSM 840).

The whiteness index was determined in the CIELAB color space from diffuse reflectance measurements according to ISO 105-J01:1997 and ISO 105-J02:1997, by using the CIE formula [14].

$$W_{10} = Y_{10} + 800(x_{n,10} - x_{10}) + 1700(y_{n,10} - y_{10}) \quad (7)$$

where: Y_{10} is the tri-stimulus value for the sample, x_{10} and y_{10} the color coordinates for the sample as this calculated using the illuminant/observer condition, $x_{n,10}$ and $y_{n,10}$ are the color coordinates of the achromatic point.

The tensile strength was measured according to ISO 13934-1:1999 [15].

3 RESULTS AND DISCUSSION

Preliminary electrolysis conducted in the filter-press cell in the absence of fabric showed that the pH rapidly rises from neutral to 9.0-9.5 during the experiment. As expected, the pH levelling-off within this basic range was also observed in the presence of fabrics. According to Figure 1, hypochlorite is therefore the prevalent chlorine species in the electrogenerated bleaching liquor, and hypochlorous acid remains at negligible amounts.

The concentration of electrogenerated active or free chlorine was also monitored during the electrolysis time at 1 A (Figure 2). It is shown that the active chlorine concentration rises during the course of the electrolysis and it reaches a steady value of about 3 g/L after six hours of treatment.

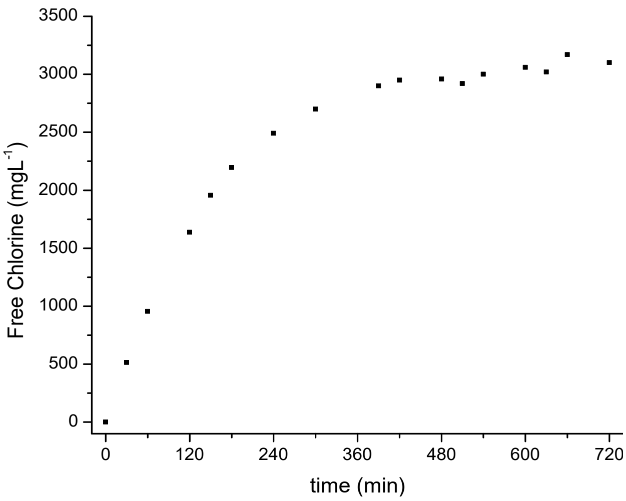

Figure 2 Evolution of free chlorine during electrolysis at an applied current of 1A

These preliminary results reveal that electrobleaching works under alkaline pH like conventional hypochlorite-based bleaching, but at lower average active chlorine concentration.

Table 1 shows the change in whiteness index of raw cotton fabrics after two hours of processing for different kind of treatments. Note that the amount of wetting agent used in the electrochemical treatment is ten times lower than in a conventional treatment.

Table 1 Whiteness index and tensile strength loss

Wetting agent concentration	Conventional treatment	Electrochemical treatment Current 0.5 A	Electrochemical treatment Current 1.0 A	Tensile strength loss [%]
0.2 % v./v.	71±2			16±2
0.0 % v./v.		35±7	57±8	6±3 (*)
0.02 % v./v.		67.1±0.7	72.3±0.3	11±2(*)

(*) This values belong to an electrochemical treatment with an applied DC current of 1.0 A.

A high whiteness index was obtained in the electrochemical process when the wetting agent was used. This value was very similar than that reached in a conventional treatment, but it has the advantage of using a considerably lower concentration of wetting agent. Moreover, a significantly lower amount of bleaching agent is generated, which would imply considerable savings in chemical costs and reduction of wastes.

Another key advantage of the electrochemical method over the conventional one is that the electrolyte can be reused for bleaching of several cotton fabrics in batchwise mode. The bleaching action of hypochlorite is related to the reaction in Eq. 6. Thus, in the electrochemical process the chloride precursor is regenerated during the bleaching action itself, which potentially enables the electrolytic bath to be used indefinitely. To illustrate this behaviour a set of experiments were designed where a series of up to 6 identical cotton fabric samples were sequentially electrobleached in the same electrolyte with no further addition of sodium chloride. Each experiment was carried out for two hours.

Figure 3 shows the evolution of the whiteness index for different cotton fabrics in batchwise mode in the same electrolyte. When working without the wetting agent, acceptable whiteness index is reached only at the fourth fabric.

The rising shape of the WI curve in Figure 3 can be related to the continuous increase in the concentration of electrogenerated active chlorine throughout the whole batch process (Figure 2).

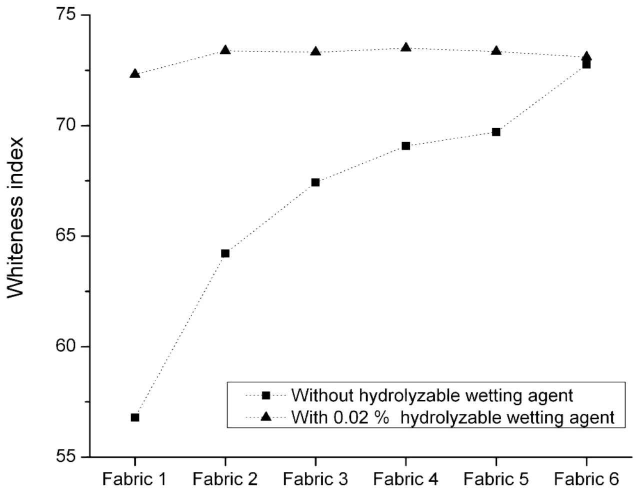

Figure 3 Whiteness index of different raw cotton fabrics electrobleached in batchwise mode with reutilization of electrolyte. A DC current of 1 A was applied in all treatments

However, when a wetting agent is added, the whiteness index is satisfactory and very similar for all the fabrics. Despite maximum steady free chlorine concentration was not yet achieved until the end of the experiment, the wetting agent enables a facile access of the electrogenerated bleaching agent to the fiber, so enhancing the bleaching rate and providing high whiteness indices.

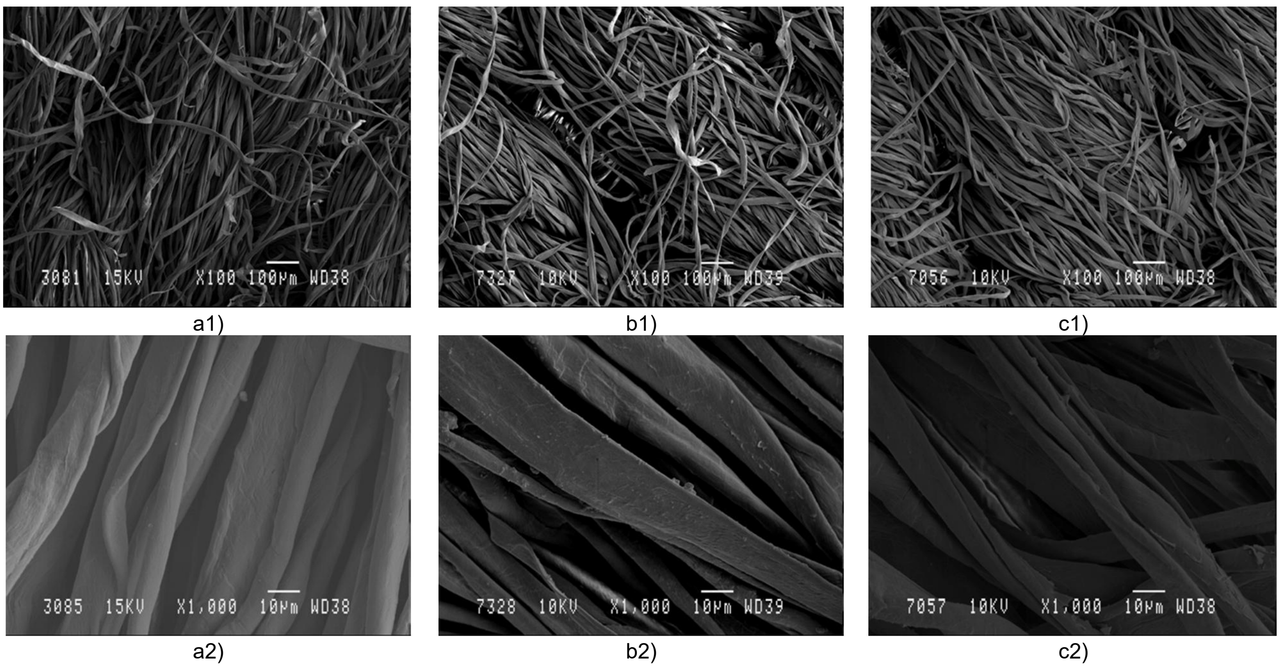

Figure 4 SEM imaging which represent a1) raw fabric x100, a2) raw fabric x1000, b1) conventional treatment of chemically bleach x100, b2) conventional treatment of chemically bleach x1000, c1) electrochemical treatment (current applied 1.0 A) x 100, c2) electrochemical treatment (current applied 1.0 A) x 1000

SEM imaging of fabrics with electrobleaching treatment did not show any noticeable change in their surface morphology. When these images are compared with those of chemically bleached fabrics we cannot observe any prominent difference between fibers. With both treatments, the fiber appearance of twisted flat ribbons with cellulose fibrils assembled in spiral along the fiber axis and the cross-sectional bilateral structure was preserved (Figure 4, a2-b2-c2). So, the electrochemical treatment produces the same surface properties as the conventional treatment.

It is well known that bleaching treatments reduce traction resistance of the fibers. With the conventional treatment there is a tensile strength loss of 16% (Table 1). On the contrary, lower losses of the tensile strength were measured in electrobleached cotton fabrics (Table 1). So, it is observed how the fabrics submitted to electrolysis had a better traction resistance than those submitted to conventional treatments.

4 CONCLUSIONS

Electrochemical technologies have shown to be methodologies of enormous potential for bleaching textiles. Electrobleaching processes based on the generation of a bleaching agent from the electrochemical conversion at an electrode of a dissolved precursor gather unequalled benefits over conventional chemical bleaching methods from economic and environmental points of view: the primary reactant, the electron, is cheap, clean, widely available and easily transferrable; in addition the bleaching species is produced on demand from a harmless precursor and its dosage can be easily set with precise control of the applied current. Therefore, transport, storage and handling of hazardous chemical can be avoided, and chemical cost reduced.

In this paper we show that raw cotton fabrics can be electrobleached by the anodic generation of hypochlorite to reach high wihiteness index, negligible affection to the fiber morphology or to the tensile strength and with the use of low concentration of wetting agents. Furthermore, the bleaching liquor is continuously regenerated which enables the use of the same electrolytic bath in the batch processing of successive cotton samples. This makes electrobleaching a environmentally friendly technology when compared to conventional chemical bleach.

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